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RELATIONSHIPS BETWEEN CONDUCTIVITY AND RESIDUES ON EVAPORATION FOR TWO GREAT LAKES WATERS

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Submitted as partial fulfillment of the requirements for the degree of Master of Science in Oceanography

Abstract

Samples from southern Lake Michigan and western Lake St. Clair were analyzed for electrical conductivity and for total and filterable residue on evaporation. For southern Lake Michigan the total residue (dried at 103-107°C) was nearly constant at 150 ppm and was almost entirely filterable. Conductivities ranged from 257 to 275 micromhos/cm at 25°C. Lake St. Clair total residues ranged from 124 ppm at the mouth of the St. Clair River to 412 ppm in the mouth of the Clinton River. Corresponding conductivities were 214 and 679 micromhos/cm.

The average ratio of conductivity to total residue was 1.72 for Lake Michigan and 1.55 for Lake St. Clair, whereas the ratios of conductivity to filterable residue were 1.76 and 1.81 respectively. These ratios were also expressed as equivalent conductances. Temperature correction coefficients were determined so that the conductances and various ratios could be converted to 18°C.

These ratios were desired for two reasons; firstly, for interpreting existing data and interpolating missing points. Secondly, these ratios allow the calculation of density for use in the dynamic height method of current determination from conductivity, temperature, and pressure data.

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RELATIONSHIPS BETWEEN CONDUCTIVITY AND RESIDUES ON EVAPORATION FOR TWO GREAT LAKES WATERS

INTRODUCTION

Residue on Evaporation

The total amount of residue found by evaporation of a water sample is a useful indicator of the total amount of dissolved chemicals and suspended matter in the sample. If suspended material is filtered out before evaporation, the filterable portion of the total residue is obtained. The nonfilterable portion can be found indirectly by the difference of the filterable and total residues, or can be determined directly by drying and weighing the filter before and after filtration.

In the past it has been common to speak of filterable and nonfilterable residues as the total dissolved and the total suspended solids respectively. Due, however, to the poor distinction between solution and suspension and to a slight loss of chloride and nitrate on heating of the residue, the terms filterable and nonfilterable residue are more precise.

Conductivity

The electrical resistance, R, of a homogeneous conductor is directly proportional to the length of the conductor, ℓ , and inversely proportional to the cross sectional area, α . If we let ρ be the proportionality constant,

$$R = \rho \frac{\ell}{a}$$
 (Eq. 1)

The constant f is a property of the conducting material and is independent of the geometry of the conductor. It is usually termed the resistivity or specific resistance. By taking the reciprocals of both sides of the above equation, we obtain the conductance, L.

$$L = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{\alpha}{2}$$
 (Eq. 2)

If we make the substitution

$$\frac{1}{\rho} = K$$
 .= conductivity or specific conductance
then $K = \frac{Q}{QR}$ (Eq. 3)

The units of conductivity are micromhos per centimeter $(\mu mhos/cm = mhos \times 10^6/cm)$. Due to the variation of conductivity with temperature, it is necessary to specify the temperature of measurement.

At low concentrations of dissolved electrolytes, the conductivity is roughly proportional to the concentration. A typical curve might be the following



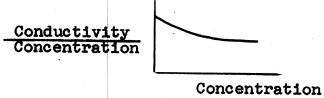
Concentration of dissolved electrolytes

By plotting instead the ratio of conductivity to concentration

as a function of the concentration, deviations from strict

proportionality between conductivity and concentration can

easily be seen.



The ratio of conductivity to concentration is known as the equivalent conductance, \bigwedge .

The factor of 1000 functions only to scale the magnitudes to convenient size.

Most strong electrolytes show nearly constant or slowly decreasing equivalent conductance as a function of concentration whereas weak electrolytes show a sharply decreasing equivalent conductance with increasing concentration. Potter (1961) gives curves for many common electrolytes.

Kohlrausch (1898) introduced the method of plotting equivalent conductance as a function of the square root of the concentration, causing the curves of equivalent conductance to become straighter at low concentrations. This introduction of a square root relationship of equivalent conductance with concentration was later justified theoretically by Debye and Hückel (1923) and Onsager (1926, 1927) in the theory of interionic attraction.

Empirical Ratios

Several authors have assumed a linear relationship between filterable residue and conductivity. Hem (1959) reports that the ratio

is between .55 and .75 for waters of normal composition. Howard (1933) lists the ratio

conductivity in mhos x 105 at 25°C

as being between 5.1 and 7.8 for selected river and well waters. Taking the reciprocals and adjusting the units to be mhos/cm per ppm, Hem's ratios become 1.33 to 1.82 while Howard's ratios are 1.28 to 1.92.

It should be noted that these empirically determined ratios are similar in nature to equivalent conductances, except for an appropriate dimensional conversion factor. If the dissolved material can be assumed to be $CaCO_3$, this factor is 50 grams per equivalent weight. Howard's data can be converted directly. Hem's ratio, involving filterable residue instead of the sum of constituents, must first be corrected to account for the conversion of bicarbonate (HCO_3) to carbonate (CO_3) during evaporation (Howard, 1933).

The ratio of conductivity to total residue includes not only the effects of dissolved electrolytes but also effects due to suspended matter such as plankton, finely dispersed silt, and other material. Due to local geographical and seasonal variations in these factors this ratio would not be expected to be constant for any large region. If, however, exact results are not demanded, useful approximations can be made.

It was thought desirable for two reasons to attempt to evaluate this empirical ratio of conductivity to total residue. First, due to the scattered and incomplete nature of data on the chemical history of the Great Lakes, such a relation would be useful in interpreting the older data and interpolating missing points. Beeton (1957) established

a relationship of this type between light penetration of surface water in Lake Huron and Secchi disc depth. This allowed older Secchi disc measurements to be interpreted in terms of a more precisely defined variable: percentage of surface light.

Secondly, due to the relative ease of making conductivity measurements, it was desired to estimate the total residue of a water sample from the conductivity for use in computing specific volume in the dynamic height method of calculation of currents in the Great Lakes (Ayers, 1956). Since the percentage change of density in the range of total residues normally encountered in the upper Great Lakes is less than 5% of the change due to normal temperature variations, the relation of conductivity and total residue can be approximate.

Seasonal variations in this ratio were thought to be of the order of ± 10%. For the intake water at the Chicago, Illinois, South District Filtration Plant since 1950, the ratio of conductivity at 25°C to filterable residue had a mean value of 1.758 (equivalent conductance 87.6) and a sample standard deviation of 0.151 whereas the ratio of conductivity to total residue had a mean of 1.638 and a standard deviation of 0.177. The filterable residue ratio had the lower deviation and hence was the more constant of the two as expected. Data from the open lake would presumably have lower deviations due to the lack of shore current and river variability and more uniform plankton and

other suspended matter distribution.

To determine these ratios for the southern basin of Lake Michigan sampling was carried out as a part of a supporting project during the summer and fall of 1962. Samples were also collected from western Lake St. Clair to obtain a broader range of conductivity and total and filterable residue values. The ratios determined were plotted versus the square root of the concentration in a manner analogous to that for equivalent conductance.

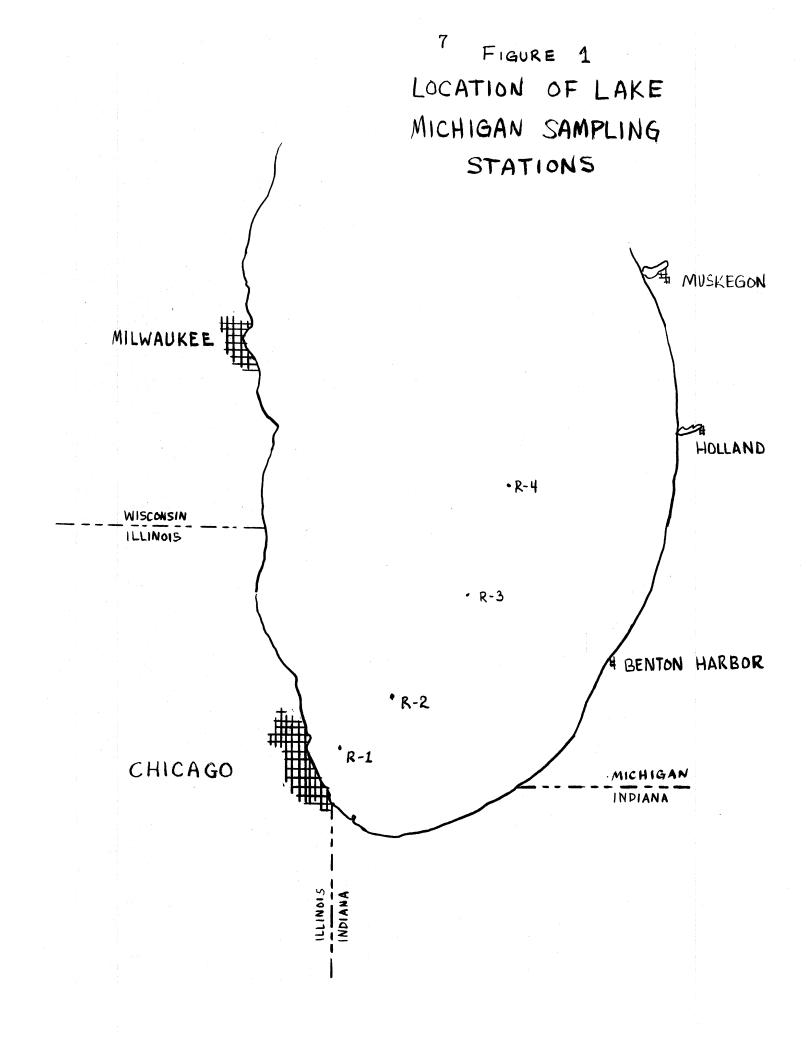
EXPERIMENTAL METHODS

Samples

Samples were taken from the R/V INLAND SEAS on August 7, August 22, September 26, and October 24, 1962, from various depths at four stations in southern Lake Michigan. The stations were approximately on a line from Chicago, Illinois, (Jackson Park) to Muskegon, Michigan, at about 3, 22, 44 and 65 miles from Chicago. The samples were taken with standard 1300 ml Nansen bottles and stored in 1 liter polyethylene bottles for periods ranging from 2 weeks to 3 months. The Lake St. Clair samples were collected from shore and from the R/V NAIAD by immersion at the surface of the 1 liter polyethylene sample bottles. Figures 1 and 2 show the sampling locations.

Total Residues

The method used to determine total residues was taken



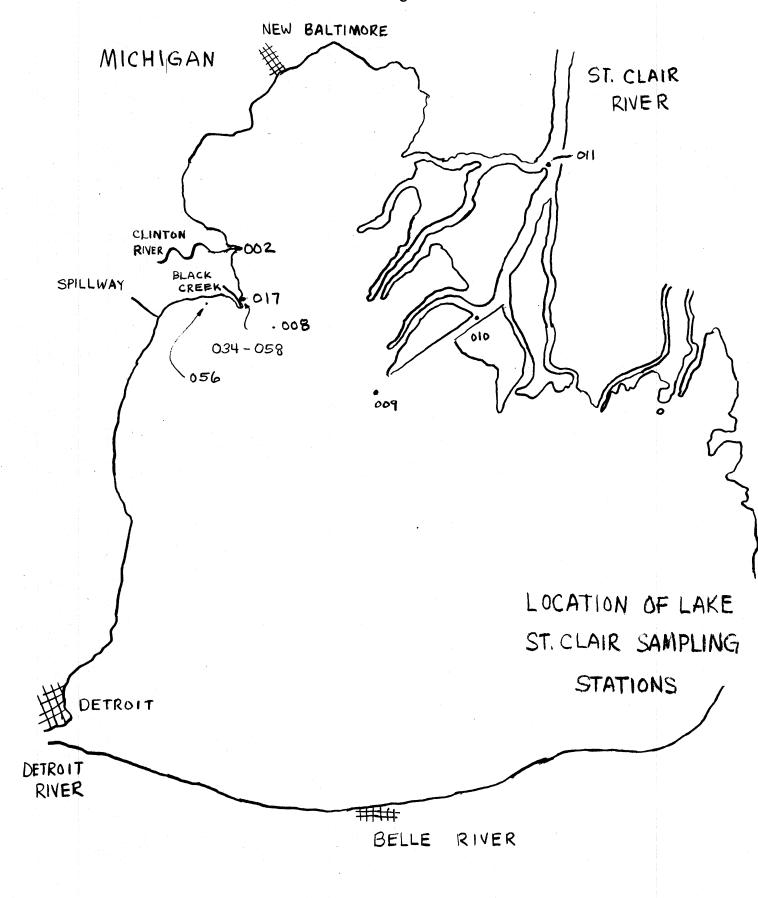


FIGURE 2

ONTARIO

LOCATION OF LAKE ST. CLAIR SAMPLES

Sample Bottle	Date Collected (1962)	Tocation	Sampled from
002 008 009 010	Oct. 17 Oct. 18 Oct. 18 Oct. 18	in Clinton River SE of Pt. Huron at end of cutoff channel in cutoff channel	R/V NAIAD R/V NAIAD R/V NAIAD R/V NAIAD
011	Oct. 18	at junction of North and South Channels	R/V NAIAD
017 056	Oct. 19 Nov. 14	<pre>in Black Creek 50 ft. off shore near west end of Metropolitan Beach</pre>	R/V NAIAD Shore
		ries of samples from Front Ran and of Pt. Huron at 50 yd. int	
058	Nov. 14	at Front Range Light (FRL) in Black Creek, at water's edge	Shore
036	Nov. 14	50 yds. SE of FRL, at water's edge	
034	Nov. 14	100 yds. SE of FRL, at water's edge	Shore Shore
035	Nov. 14	150 yds. SE of FRL, at water's edge	Shore
051	Nov. 14	200 yds. SE of FRL, at water's edge	Shore
052	Nov. 14	250 yds. SE of FRL, at water's edge	Shore
053	Nov. 14	300 yds. SE of FRL, at water's edge	Shore
054	Nov. 14	350 yds. SE of FRL, 50 ft.	Shore
055	Nov. 14	400 yds. SE of FRL, 20 ft.	
057	Nov. 14	from shore 450 yds. SE of FRL, 10 ft. from shore, (almost at	Shore
		tip of Pt. Huron)	Shore

Samples 034-058 were taken when there was a SE wind of 6-8 knots.

from Standard Methods. Two 200-500 ml samples were evaporated to dryness over a steam bath, 100 ml aliquots at a time, in previously dried and weighed 250 ml nickel evaporating dishes. Each sample was dried overnight in an oven at 103-107°C, cooled in a desiccator and weighed after 1 minute on a balance accurate to 0.1 mg. The average of the two samples was taken as the total residue. All samples gave residues in the range 25-85 mg. A secon drying overnight and weighing was performed as a check.

Several precautions were necessary to obtain accurate determinations by this method. The dishes were rinsed in dilute HCl, washed, rinsed in deionized distilled water, dried overnight, cooled, and weighed. Before pipetting, the sample was thoroughly shaken. This was especially important with the Lake St. Clair waters containing much suspended matter.

Since the residue after drying is rather hydroscopic, it can pick up moisture during cooling or weighing. In a large pyrex desiccator (250 mm diameter) containing anhydrous CaSO4, "Drierite", 45-60 minutes was found to be sufficient for cooling of the residue without noticeable moisture pickup. Longer cooling periods gave results 1-2 mgm. heavier. The cooling time had to be shortened when the room temperature was lower than normal. Small beakers of desiccant were kept in the balance during weighings.

Filterable and Nonfilterable Residue

Filterable residue was separated from the samples by Millipore filters of 47 mm diameter and 0.80 micron pore size. Following a procedure similar to that for total residues. Insufficient sample volume necessitated limiting the determination to only one sample. As a check on the accuracy of the determinations, in several cases the filters were weighed to give the nonfilterable residue which was then added to the filterable portion and compared with the total. This was not done regularly as the amounts of non-filterable residues in Lake Michigan samples were too small to be of significance whereas Lake St. Clair nonfilterable residue samples did not dry to constant weight in a reasonable time at 103-107°C.

Precision of Residue Measurements

The Lake Michigan total residue determinations showed an average difference of 4.4 ppm in 36 paired samples. Three samples had differences of greater than 10 ppm whereas most were with 1-2 ppm of each other.

The Lake St. Clair total residue samples had a somewhat lower precision. The average difference between individual determinations was 5.8 ppm in 16 paired samples, three showed differences of greater than 10 ppm. Since one of these latter contained fine sand in suspension, variations in pipetting the sample could account for the descrepency. Due to the nature of total residues the absolute accuracy of the determinations can not be stated, only an estimate of the precision found be repeated determinations.

Several sources of potential error in the standard method of total residue determinations became apparent during the laboratory work. These errors could be reduced in future determinations by the following modifications in procedure:

- 1. Use of a larger sample volume (1 liter for Lake Michigan samples, 200 ml to 1 liter for Lake St. Clair samples) would reduce the effect of small errors in weighing.
- 2. Determination of the sample volume accurately at the time of collection on shipboard would eliminate errors in pipetting caused by partial separation and settling of suspended matter during storage of the sample. This would require a separate sample aliquot bottle for each determination. The sample aliquot bottles would have to be rinsed with distilled water and the washings combined with the rest of the sample at the time of evaporation.
- 3. Evaporation of the samples in aluminum foil dishes under unfrared heat lamps would allow more samples to be run at a time than was possible with the steam bath used for this work. An additional advantage of aluminum foil would be the elimination of the cooling in a desiccator due to the foil's rapid cooling after removal from the drying oven.

Conductivity Measurements

All conductivity measurements were made on a Leeds and Northrup AC Wheatstone Bridge, Catalog No. 4866-60, Serial No. 1599817, using 60 cps supply voltage. A pipette type cell manufactured by Industrial Instruments, Inc., Cedar Grove, N. J., was used because of its small sample size requirements.

The bridge has a manual temperature adjustment which corrects the readings to 25°C from the temperature of measurement. Because conductivity values at 18°C were also desired. it was necessary to convert all 25°C conductivities using an appropriate temperature correction factor. To obtain this factor, the conductivity of typical water samples from Lake Michigan and Lake St. Clair were measured as a function of temperature using the method of Smith (1962). Samples were cooled in an ice bath and then warmed to 25-30°C while observing the conductivity, using a Leeds and Northrup type 130033 dip cell which was more suitable for this purpose than the pipette cell. The sample was constantly agitated by a magnetic stirrer and by the nearly completely immersed dip cell. Temperature was measured on either side of the cell by two mercury thermometers accurate to 0.1°C and averaged. When the data were plotted the values of the conductivity at 18°C and 25°C were read. The ratio of these values was taken as the appropriate conversion factor.

The accuracy of the bridge was determined to be greater than \pm 0.5% by comparison with standard resistances. The other limiting factor in the accuracy of the conductivity measurements was the lack of sufficient temperature control of the sample. This error was of the same order as the bridge accuracy. Multiplying the temperature coefficient found (2.4%/°C) by the accuracy of the temperature measurements (\pm 0.15°C), the accuracy \pm 0.35% is obtained. The conversions to 25°C and 18°C from the temperature of measurement may reduce the final accuracy of the 18°C conductivities to 1%.

Since the readings at 25°C were the more accurate of the two series and since 25°C measurements are suggested by Standard Methods, the results are based on conductivities at this temperature. Corresponding ratios at 18°C can be determined by multiplying by the following empirically determined factors.

Mul	t1]	p1	1c	at	ive
	F	ac	to	r	

Lake Michigan 0.857

Lake St. Clair 0.863

RESULTS

Lake Michigan

The data obtained for Lake Michigan are given in Appendix A. The plots in Appendix B show the vertical distribution of the various variables along the sampling line.

Because of a lack of sufficient sample volume, only two values of filterable residue are given for August 7. Station 4 was omitted on August 22.

Lake St. Clair

Because of the nature of the Lake St. Clair sampling, the data were not plotted geographically. The data are given in Appendix A. A plot of the conductivity at 25°C as a function of total and filterable residue is given, as is a plot of the ratio of the conductivity to total and filterable residue as a function of the square root of the respective residues. (Figures 3 and 4)

DISCUSSION

Lake Michigan

Due to the difficulty in obtaining consistant results during the weighing operations, sometimes the filterable residue exceeded the total residue. This was true most often in cases when the filterable and total residues were almost equal. The results were used directly, however, in the calculation of the average ratios as these averages tend to cancel out minor inconsistancies.

The results of August 7 showed a higher variability of total residue than did the later samples. These results were included in the final averages even though it was thought some of the variability might be due to weighing inaccuracies. In the later samples when the weighing technique was more refined, similar unexplained deviations also occurred. For this reason it was felt that the August 7 results should not be omitted.

The total residue on August 22 showed two regions of higher than normal concentration. These were at the bottom at Station #1 and at the surface at Station #3. The filterable residue appeared abnormally low (126 ppm) on the surface at Station #1.

On September 26 a region of high total and filterable residue was near the bottom at Stations #1 and 2.

On October 24 the distribution of total and filterable residue was quite uniform except for one anomalously high value

(177 ppm) at a depth of 145 feet at Station #3. Since this is the result of a single determination, it is questionable.

The conductivity on all occasions was quite uniform being in the range 257 to 275 mhos/cm. A few values fell outside this range.

The overall average ratio of conductivity to total residue was 1.719. This value had a standard deviation of 0.113. The average ratio of conductivity to filterable residue was 1.758 with a standard deviation of 0.105. Here the filterable ratio was slightly the more constant.

The average ratios for each of the four sampling dates are as follows:

Date	Conductivity Total residue	Conductivity Filterable residue
August 7, 1962	1.680	1.876
August 27, 1962	1.702	1.824
September 26, 1962	1.747	1.716
October 24, 1962	1.737	1.736

Similarly, the averages for each station are:

Station #1	1.721	1.824
#2 #3 #4	1.718	1.707
#3	1.695	1.733
#4	1.753	1.776

These averages show the ratio conductivity to total residue increased from August through September whereas the ratio of conductivity to filterable residue decreased during the same period. The averages for individual stations show no pronounced trends.

Lake St. Clair

Figure 3 shows that the conductivity rises as a function of the filterable residue at a slope of 1.822 to 300 ppm

where the slope falls to 1.40. The average slope or ratio is 1.810.

The conductivity shows an almost linear behavior with the total residue. Here the slope is uniform throughout the range 0 to 400 ppm at 1.603, neglecting one anomalous sample (056) which contained fine sand, causing an unusually high total residue. Including this sample reduced the average slope to 1.553.

Figure 4 is a plot of the ratio of conductivity at 25°C to total and filterable residue versus the square root of the respective residue in a manner analogous to the square root relationship due to Kohlrausch (1898). The data appear quite scattered, centering around the average values as shown. Because of the lack of sufficiently dilute samples, no meaningful curve can be drawn.

SUMMARY

The ratios presented in this paper allow the interpretation and evaluation of records on the chemical history of Lakes Michigan and St. Clair. Interpolations and extrapolations can be made using the overall averages.

For calculation of density from temperature, pressure, and conductivity data, a modification of the method of Ayers (1956) is used. This involves adding a term to the density calculation to account for the dissolved and suspended matter.

During evaporation of a total residue sample, bicarbonate (HCO_3^-) dissociates into carbonate (CO_3^-) and releases carbon dioxide gas.

$$Ca(HCO_3)_2 = Ca(CO_3) + H_2O + CO_2$$

This causes the total residue to be less than the sum of dissolved constituents and suspended matter.

If the concentration of HCO_3^- is known for the water in question, it can be divided by 2.03, the ratio of the molecular weights of $(HCO_3^-)_2$ and CO_3^- , to represent the amount of CO_3^- retained after evaporation. Hence

amount of
$$CO_3^-$$
 retained after evaporation. Hence
$$\left\{ \frac{HCO_3^-}{3} \right\} = \left\{ \frac{HCO_3^-}{2.03} \right\} \text{ or } 0.507 \left\{ \frac{HCO_3^-}{3} \right\}$$

is the weight loss per liter. Here the brackets represent concentration in parts per million.

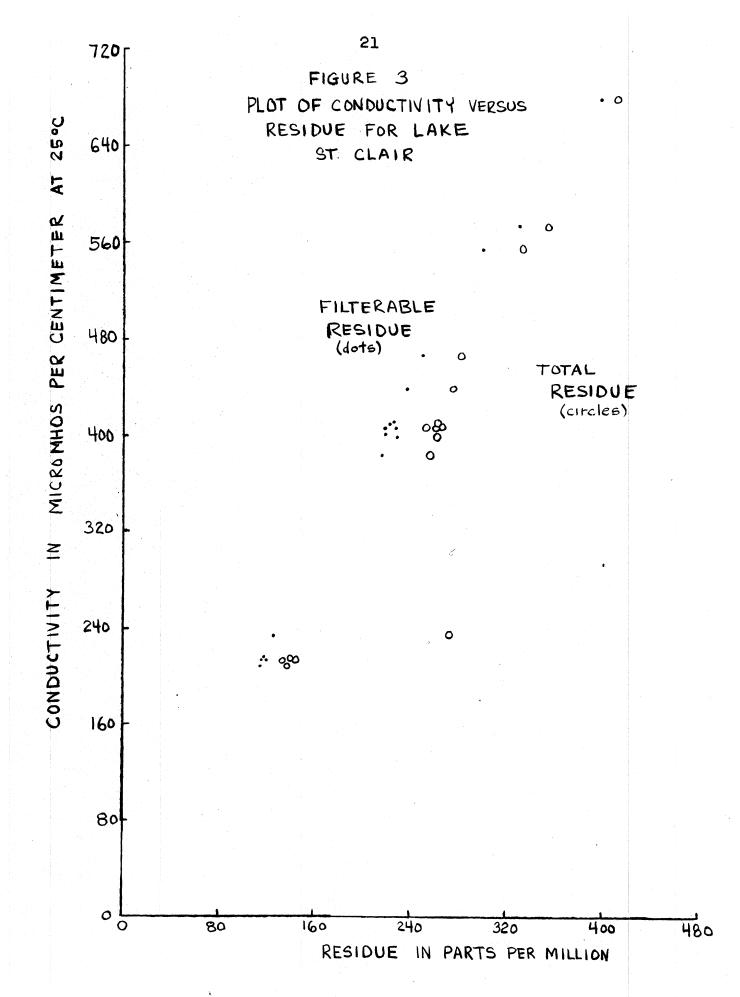
The factor

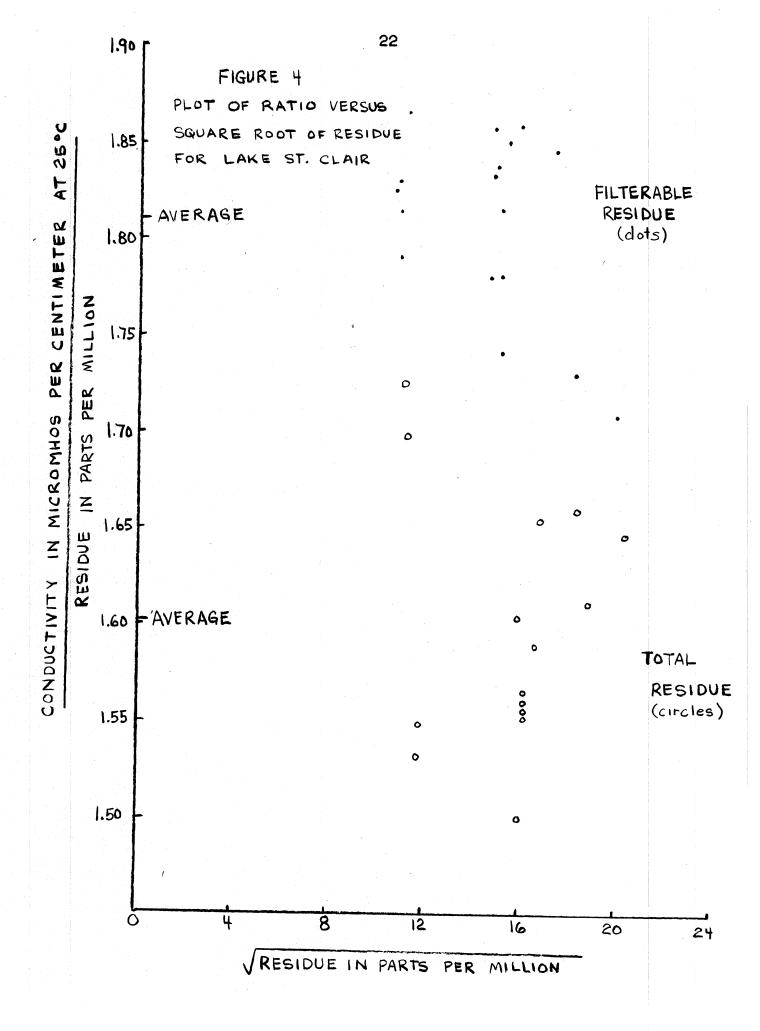
Total Residue +
$$0.507 \left\{ HCO_3^{-} \right\}$$

is then an estimate of the weight of dissolved and suspended matter in the sample. This term, in ppm or mg/l, is then added to the density obtained by Ayer's method. By using the ratios presented in this paper, this factor becomes

Small errors due to the loss of choride and nitrate during evaporation and due to neglecting the water of crystallization are assumed to be small. Since these

errors would tend to be constant over a large region, they introduce only a systematic error and would not appreciably affect dynamic height calculations.





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APPENDIX A

LAKE MICHIGAN

August 7, 1962

Sta.	Depth (ft.)	18°C Cond (Mmh	25°C Cond los/cm)	TR (ppm)	FR (ppm)		Cond FR nos/cm 25%	(ppm) ^{1/2}	(ppm) /2
1	0 15 40	230 228 228	268 266 266	150 148 145		1.786 1.799 1.834	pm	12.24 12.17 12.03	
2	0 50 164	224 225 230	262 263 269	156 171 175	146	1.680 1.538 1.538	1.793	12.49 13.09 13.21	12.09
3	0 60 322	230 229 231	269 267 270	174 167 163		1.548 1.600 1.658		13.19 12.91 12.78	
4	0 39 131 372	230 227 229	268 265 267	161 141 188 143	137	1.900 1.410 1.869	1.960	12.70 11.88 13.70 11.95	11.70
Aug	gust 22	, 1962							
1	0 26 33	230 227 236	268 265 275	149 169 164	126 133 148	1.800 1.569 1.679	2.125 1.999 1.860	12.20 13.00 12.80	11.21 11.52 12.17
2	0 66 177	224 224 230	262 261 268	139 145 151	152 151 156	1.887 1.800 1.775	1.724 1.730 1.720	11.79 12.03 12.29	12.32 12.29 12.49
3	0 43 90 294	223 223 228 229	260 260 266 267	174 178 140 162	151 152 152 152	1.495 1.462 1.900 1.650	1.724 1.712 1.750 1.758	13.20 13.34 11.82 12.72	12.29 12.32 12.32 12.32
Sep	tember	26, 19	62						
1	0 8 15	224 225 227	261 263 265	150 150 172	155 158 152	1.740 1.752 1.540	1.685 1.665 1.745	12.24 12.24 13.10	12.44 12.57 12.32
2	0 79 105 164	220 223 231 229	257 260 270 267	145 144 151 170	151 148 174 172	1.772 1.805 1.789 1.572	1.702 1.758 1.552 1.552	12.02 12.00 12.29 13.03	12.29 12.17 13.19 13.10
3	0 65 111 305	223 223 228 227	260 260 266 265	143 146 150 150	148 144 155 151	1.820 1.782 1.774 1.767	1.758 1.807 1.718 1.755	11.97 12.09 12.25 12.25	12.17 12.00 12.43 12.29
4	0 79 167 400	222 223 228 228	259 260 266 266	146 146 152 149	149 147	1.775 1.780 1.750 1.785	1.739 1.770 1.773 1.762	12.09 12.09 12.32 12.20	12.20 12.12 12.25 12.29

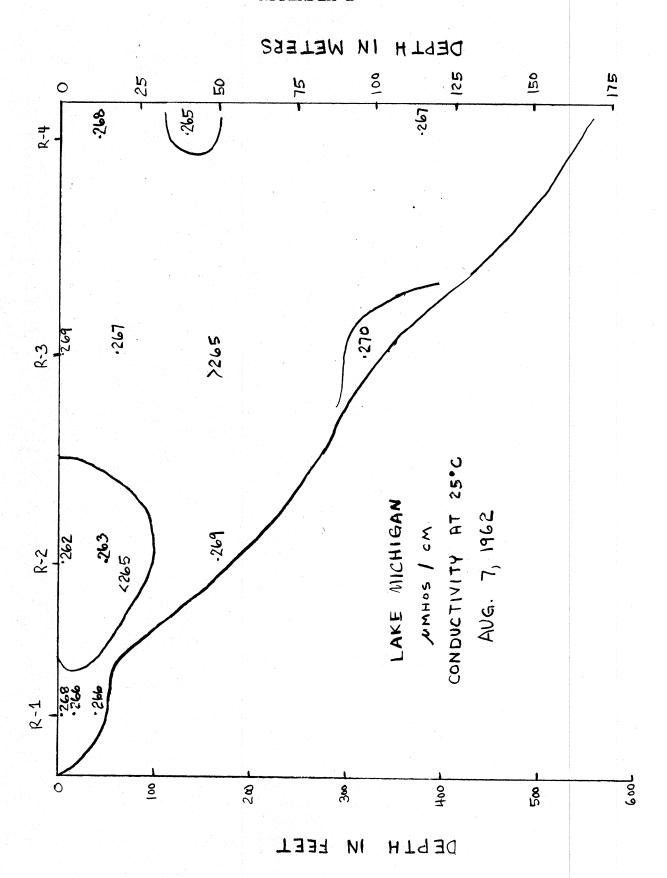
LAKE MICHIGAN
October 24, 1962

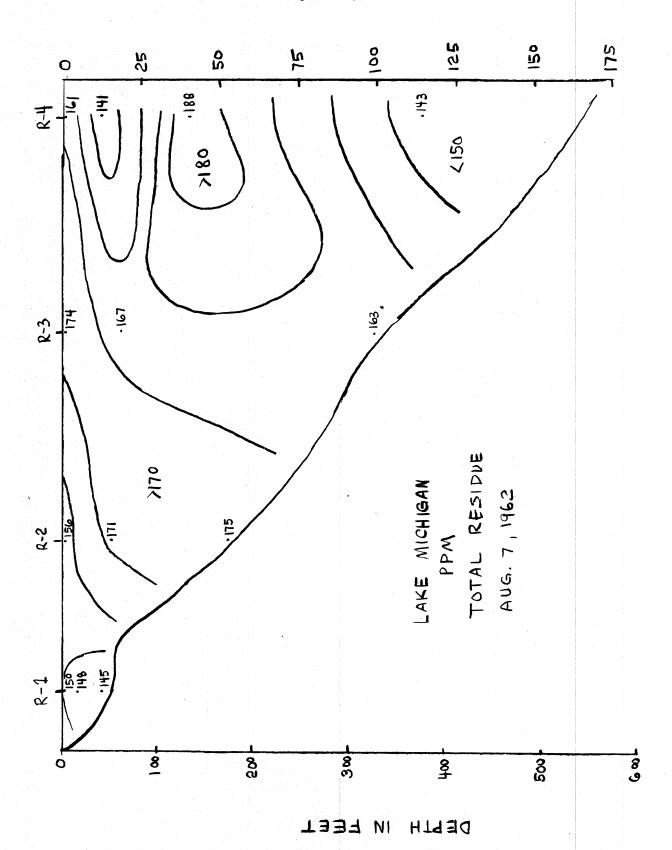
Sta.	Depth (ft.)	18°C Cond (/ Mmho	25°C Cond os/cm)	TR (ppm)	FR (ppm)		Cond FR os/cm 25° pm	TR c)(ppm)/2	(ppm) ^{1/2}
1	0	229	267	156	150	1.712	1.780	12.50	12.25
	18	229	267	155	154	1.725	1.735	12.43	12.40
2	0	223	260	150	149	1.732	1.748	12.25	12.20
	92	224	261	152	152	1.723	1.723	12.32	12.31
	1 45	230	268	156	151	1.719	1.777	12.50	12.29
3	0	224	261	152	146	1.719	1.789	12.32	12.09
	87	226	264	151	150	1.750	1.760	12.29	12.23
	1 45	227	265	155	177	1.711	1.500	12.43	13.30
	309	229	267	150	151	1.781	1.770	12.25	12.29
4	0	224	262	149	150	1.760	1.749	12.20	12.24
	98	224	261	148	150	1.765	1.740	12.17	12.24
	157	227	265	152	154	1.746	1.721	12.32	12.40
	381	230	268	154	151	1.740	1.775	12.40	12.29

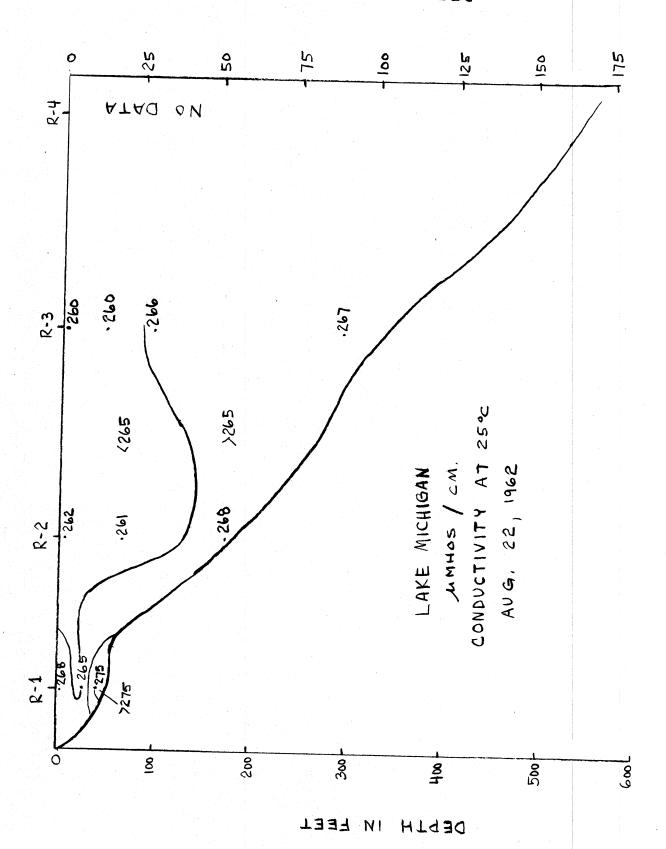
LAKE ST. CLAIR Surface Water

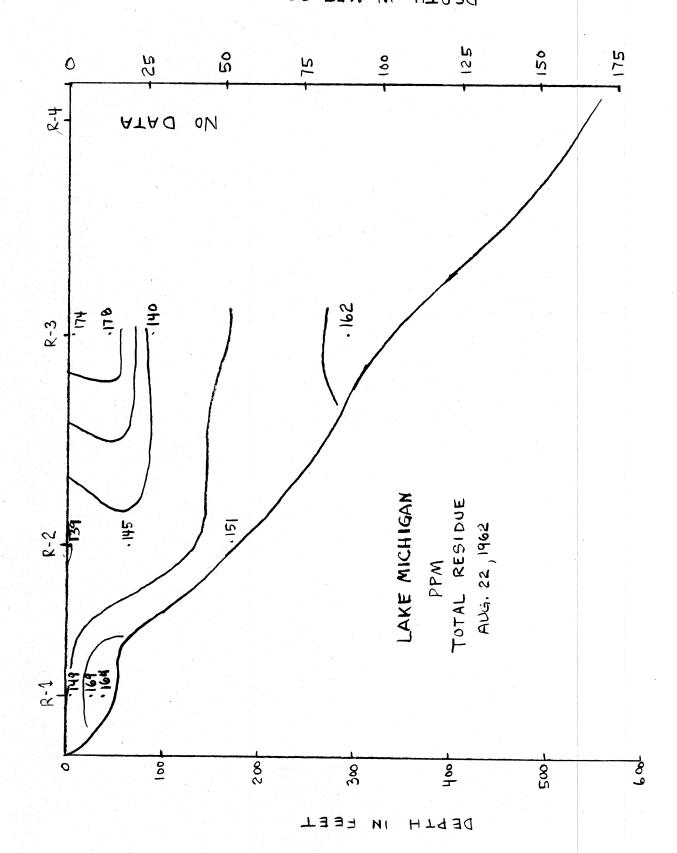
Sample						
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APPENDIX B

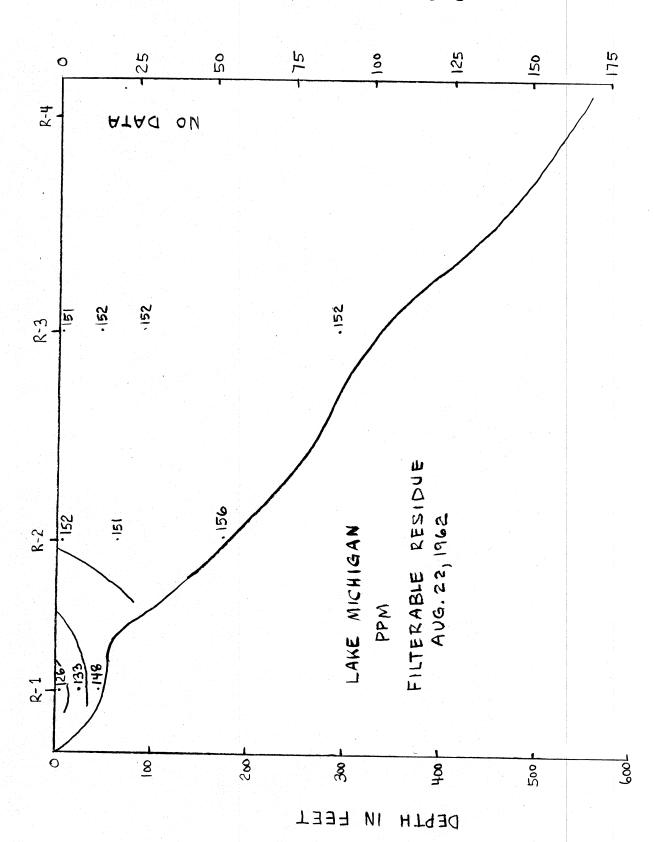


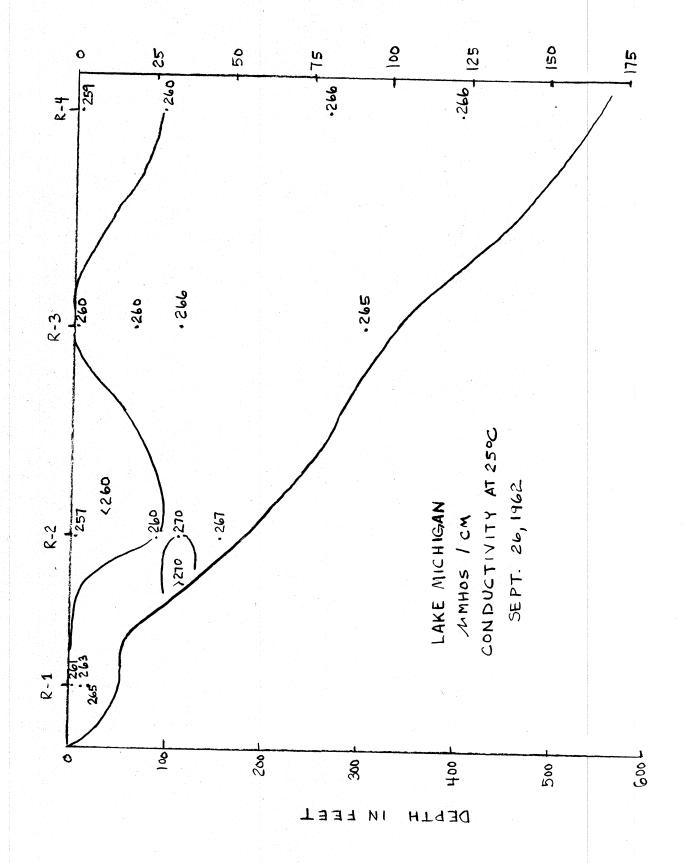


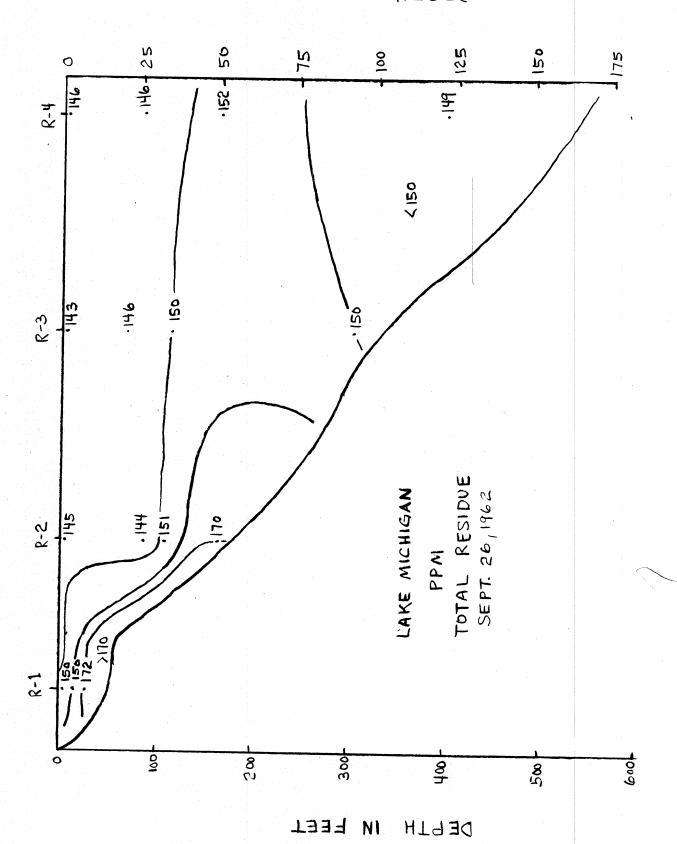


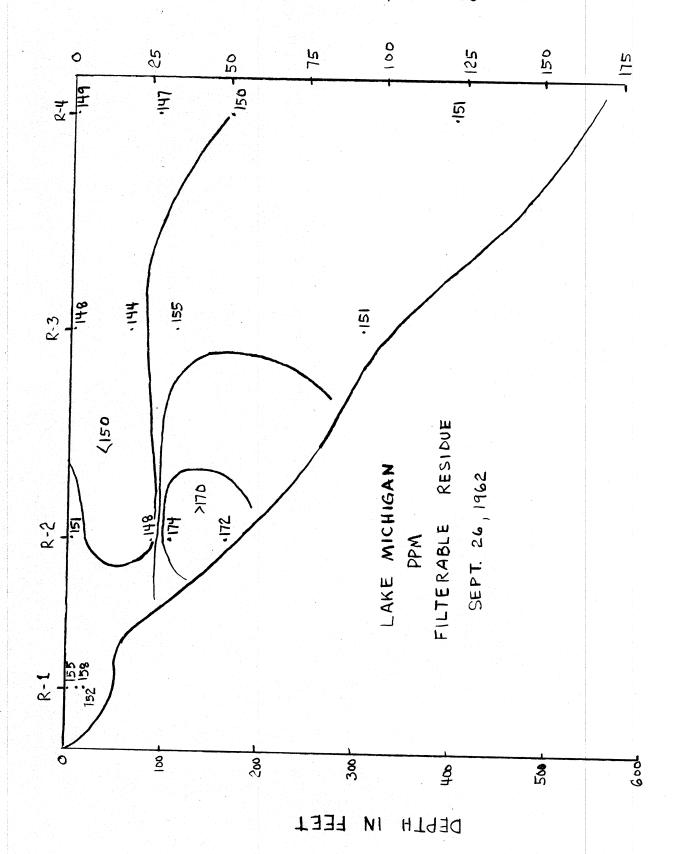


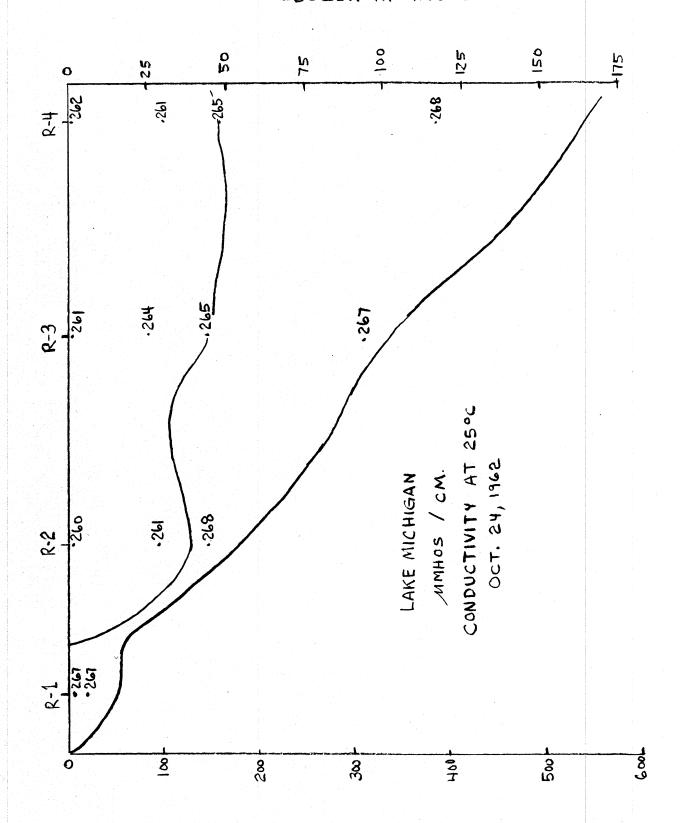
DEPTH IN METERS



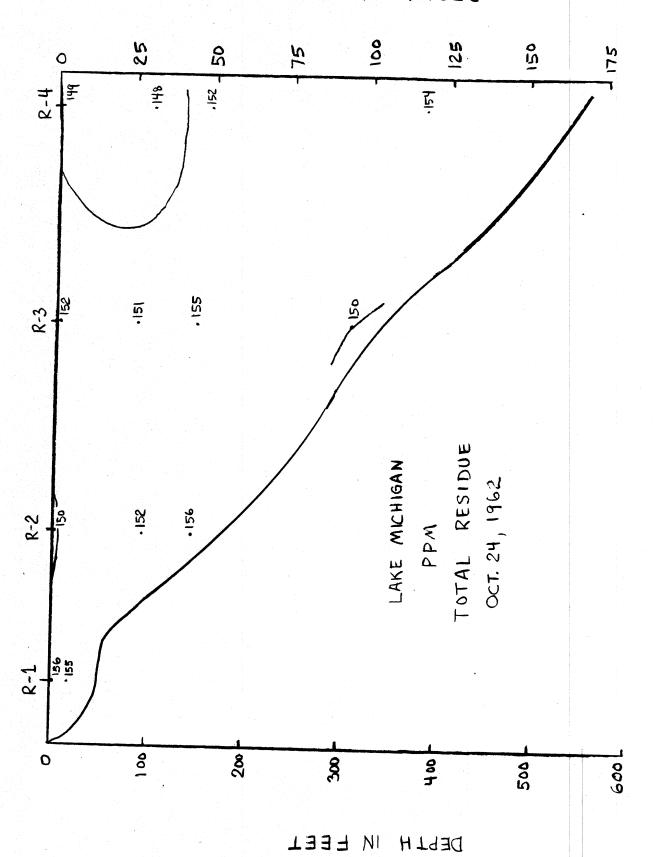


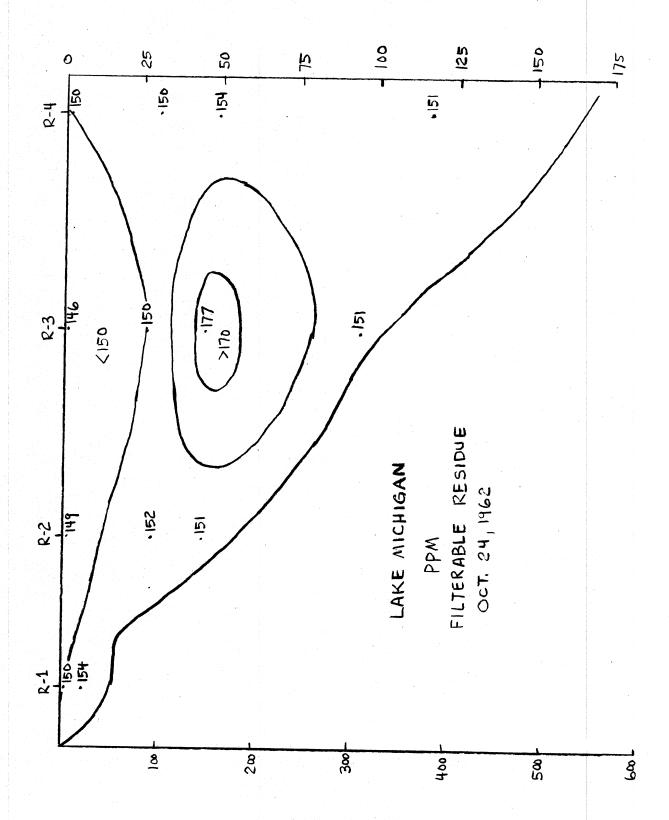






DEPTH IN FEET





DEPTH IN FEET